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(1)

- AN - 1990-003003 [01]
- TI - Modified polyethylene resin prefoamed particles prepn. - by dispersing polyethylene resin, vinyl aromatic monomer and polymerisation initiator in aq. medium, heating, treating with foamer
- AB - The process comprises dispersing (1) 100 pts. wt. of polyethylene type resin particles, 5-300 pts. wt. of vinyl aromatic monomer and 1.0-3.0 pts. wt. (to 100 pts. wt. of the monomer) of polymerisation initiator in aq. medium, (2) heating the dispersion to temp. up to the temp. causing polymerisation of the monomer to impregnate the monomer into or on the surface of the polyethylene type resin particles, (3) increasing the temp. of the aq. dispersion to polymerise the monomer, (4) impregnating volatile foaming agent during or after the polymerisation and then (5) foaming the resin particles.
 Pref. amt. of the vinyl aromatic monomer is pref. 30-200 pts. wt. to 100 pts. wt. of the polyethylene type resin particles. Amt. of the polymerisation initiator is 1.1-2.0 pts. wt. to 100 pts. wt. of the vinyl aromatic monomer. The polyethylene type resin is powder or pellet with mean particle size 0.05-5 mm. Vinyl aromatic monomer is styrene, methyl-styrene, dimethyl styrene, etc. opt. in mixt. of blend with copolymerisable monomer, e.g. acrylonitrile, (meth)acrylic acid ester, divinyl benzene, mono- or dialkyl maleate, etc. Polymerisation initiator is organic peroxide, e.g. benzoyl peroxide, lauroyl peroxide, etc. of azo cpd., e.g. azoisobutyronitrile, azobisdimethyl valeronitrile etc. Suspending agent is PVA alcohol, polyvinyl pyrrolidone, etc. Volatile foaming agent is e.g. n-propane, n-butane, cyclobutane, methyl chloride, etc.
- USE/ADVANTAGE :
 The resin particles can be used as cushioning material, packaging material, vessel, etc., because the particles can be heat foamed to give mouldings with good rigidity and impact resistance.
- IW - MODIFIED POLYETHYLENE RESIN PREFOAM PARTICLE PREPARATION DISPERSE VINYL AROMATIC MONOMER POLYMERISE INITIATE AQUEOUS MEDIUM HEAT TREAT FOAM
- PN - JP1284536 A 19891115 DW199001
 JP2668384B2 B2 19971027 DW199748
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Notes:

1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

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FULL CONTENTS

(57) [Claim(s)]

[Claim 1] The polymerization initiator of a 1.0 – 3.0 weight part is distributed in an aqueous medium to the straight chain-like low-density-polyethylene resin particle 100 weight part non-constructed a bridge, the vinyl aromatic series monomer 5 – 300 weight parts, and this monomer 100 weight part. After heating to the temperature which the polymerization of this monomer does not start substantially and making this monomer sink into the inside and the surface of said polyethylene system resin particle, The polymer particles which the temperature of the above-mentioned water soil suspension was raised, and polymerized this monomer and in which the vinyl aromatic series polymer of 0.05–0.1 micrometer of mean particle sizes carried out micro distribution into this polyethylene system resin particle are obtained. The manufacture method of the property modification polyethylene system resin foaming fabrication object characterized by being filled up with the preliminary foaming particles which the volatile foaming agent was made to sink into said polymer particle, were made to foam during a polymerization or after the end of a polymerization, and were obtained in a metallic mold, carrying out heating weld, and acquiring a foaming fabrication object.

[Claim 2] The manufacture method according to claim 1 that a vinyl aromatic series monomer is a 30 – 200 weight part to the straight chain-like low-density-polyethylene resin particle 100 weight part non-constructed a bridge.

[Claim 3] The manufacture method according to claim 1 or 2 that a polymerization initiator is a 1.1 – 2.0 weight part to a vinyl aromatic series monomer 100 weight part.

[Claim 4] The manufacture method according to claim 1, 2, or 3 that the density of a foaming fabrication object is [a Charpy impact value] 1.0 or more 19g / above **.

[Detailed Description of the Invention]**[Industrial Application]**

This invention relates to the manufacture method of the rigid and shock-proof extremely excellent property modification polyethylene system resin foaming fabrication object in more detail about the manufacture method of the straight chain-like low-density-polyethylene resin foaming fabrication object for which a bridge is not constructed [by which property modification was carried out].

[Description of the Prior Art]

Generally, the foaming object of polyethylene system resin has the strong point of elasticity being high and excelling in oil resistance and shock resistance other than the feature that distorted recuperative strength is large, also to repeated stress, and is widely used as important labeling and packaging materials. However, preliminary foaming particles, nothing, and this are fabricated for polyethylene system resin particles in a model. When acquiring a foaming fabrication object, it is easy to start contraction of the preliminary foaming particle or the foaming fabrication object after the fabrication in a model from the rigid lowness of polyethylene, and has the demerit in which the acquired foaming fabrication object is soft and compressive strength is low.

How to polymerize by infiltrating a PINIRU aromatic series monomer into polyethylene system resin as how to improve such a fault, and to obtain property modification polyethylene system resin preliminary foaming particles are a JP,45-32623,B number, 51-46138, 52-10150, 59-3487, etc. It is proposed.

However, since sinking in and the polymerization to polyethylene system resin of a vinyl aromatic series monomer are performed in simultaneous parallel by these methods, There is a problem that this monomer of quantity that cannot be disregarded before heterogeneity arises in a polymerization reaction in the

particle surface and Uchibe, and the homogeneity of generation particles is inferior as a result and polyethylene system resin sinks in will polymerize as independent particles.

In order to solve these problems, it is at a JP,58-53003,B number, 58-51009, and 58-51010, When the sinking-in polymerization of the polymerization initiator of a 0.01 - 0.8 weight part is carried out to a vinyl system monomer and this monomer 100 weight part at polyethylene system resin particles, After decomposition of a polymerization initiator infiltrates this 80% or more of monomer at the temperature which is not started substantially, the method of polymerizing by raising temperature is indicated.

According to this method, the homogeneity of generation particles improves and it is indicated by separating a sinking-in process and a polymerization process that the independent polymer of a vinyl system monomer does not generate as a matter of fact.

Moreover, although the method of carrying out the sinking-in polymerization of the styrene monomer is indicated in the JP,62-59642,A number at high-density polyethylene system resin particles, it is necessary to use the bridge-constructed particles of 10 to 40% of the rate of a gel part.

[Problem(s) to be Solved by the Invention]

The generation particles obtained like the above by carrying out the sinking-in polymerization of the vinyl system monomer at polyethylene system resin particles, Although it has the sea island structure which vinyl system polymer particles are distributing in the matrix of polyethylene system resin When based on said conventional technology, rigidity and shock resistance may not satisfy the foaming fabrication object acquired by bridge-constructing being required, and the diameter of a distributed particle of a vinyl system polymer being large, carrying out preliminary foaming of these generation particles, and carrying out hot forming further.

[Means for Solving the Problem]

By this invention, it excels in the shock resistance which is the character of polyethylene system resin original. And it aims at manufacturing the property modification polyethylene system resin foaming fabrication object which improved rigidity. 1.0-3.0 weight part use of the quantity of the polymerization initiator which a vinyl aromatic series monomer is polymerized to the straight chain-like low-density-polyethylene resin particles non-constructed a bridge, and is sold to them is carried out to this monomer 100 weight part, and the diameter of a distributed particle of the vinyl aromatic series polymer in generation particles is made small. Therefore, the method of manufacturing the cast equipped with the outstanding shock resistance and rigidity is offered.

This invention Namely, the straight chain-like low-density-polyethylene resin particle 100 weight part non-constructed a bridge, The polymerization initiator of a 1.0 - 3.0 weight part is distributed in an aqueous medium to the vinyl aromatic series monomer 5 - 300 weight parts, and this monomer 100 weight part. After heating to the temperature which the polymerization of this monomer does not start substantially and making this monomer sink into the inside and the surface of said polyethylene system resin particle, The polymer particles which the temperature of the above-mentioned water soil suspension was raised, and polymerized this monomer and in which the vinyl aromatic series polymer of 0.05-0.1 micrometer of mean particle sizes carried out micro distribution into this polyethylene system resin particle are obtained. The manufacture method of the property modification polyethylene system resin preliminary foaming particles characterized by being filled up with the preliminary foaming particles which the volatile foaming agent was made to sink into said polymer particle, were made to foam during a polymerization or after the end of a polymerization, and were obtained in a metallic mold, carrying out heating weld, and acquiring a foaming fabrication object is made into the contents. It is.

The straight chain-like low density polyethylene for which a bridge is not constructed [which is used in this invention] has the desirable copolymer of ethylene and an alpha olefin. 1-BUTEN [for example,], 1-pentene, 1-HEKISEN, 3, and 3-*****- 1-BUTEN, 4-*****- 1-pentene, 4, and 4-*****- 1-pentene, 1-OKUTEN, etc. are mentioned as an alpha olefin. Moreover, it is even if it uses together low density polyethylene, high-density polyethylene, an ethylene propylene copolymer, an ethylene propylene butene-1 copolymer, an ethylene-vinyl acetate copolymer, an ethylene acrylic acid copolymer, ethylene VCM/PVC copolymers, and these two sorts or more in a little ranges. It is good.

As for form, it is desirable that it is in particle states, such as powder and a pellet type. The average particle diameter is a range with about 0.05-5 suitablemm. When the big particles which **** of a foaming agent is intense and exceed 5mm when smaller than 0.05mm are used, the distribution at the time of a polymerization is difficult, and since the restoration nature at the time of fabrication worsens, it is not desirable.

As the vinyl aromatic series monomer used in this invention, Besides styrene, MECHIRU styrene, JIMECHIRU styrene, ethyl styrene, alpha-substitution styrene, such as nucleus substitution styrene,

such as iso pro pill styrene and KURORU styrene, and alpha-methylstyrene, etc. Independent or two or more sorts of mixtures, Or as for the above-mentioned monomer, a little other copolymerizable monomers, for example, acrylonitrile, acrylic ester, methacrylic acid ester, JIBINIRU benzene, and maleic acid mono-****, a mixture with JIARUKIRU and others is used.

the quantity of a vinyl aromatic series monomer receives the straight chain-like low-density-polyethylene resin 100 weight part non-constructed a bridge — a 5 - 300 weight part — it is a 30 - 200 weight part preferably. If 300 weight parts are exceeded, since a vinyl aromatic series monomer all is not uniformly absorbed by this straight chain-like low-density-polyethylene resin but the monomer which is not absorbed polymerizes independently, it is not desirable. Moreover, the straight chain-like low-density-polyethylene resin which absorbed the vinyl aromatic series monomer so much results in losing character peculiar to straight chain-like low density polyethylene. On the other hand, since [that under 5 weight parts of a rigid improvement of straight chain-like low-density-polyethylene resin are enough as a vinyl aromatic series monomer] it is not carried out, it is not desirable.

As a polymerization initiator used in this invention, what is generally used as an initiator for suspension polymerization of a vinyl aromatic series monomer can be used as it is. For example, benzoyl peroxide, lauroyl peroxide, t-butyl peroxide, tert-butyl peroxide benzoate, 1, and 1-screw 3, 3, 5-bird MECHIRUSHIKUROHEKISAN, (Tert-butyl peroxide) Organic peroxide, such as t-butyl peroxide ISOPUOPIRU carbonate, 2, and 2-bis(tert-butyl peroxide) butane and dicumyl peroxide; they are azo compounds, such as azo-isobutyro-dinitrile and azobis dimethylvaleronitrile, etc. these polymerization initiators are independent — two or more sorts may be used together and you may use again. The polymerization initiator should be oil-soluble nature, make it dissolve in a vinyl aromatic series monomer, or makes a polymerization reaction dissolve trouble in a little dirty solvents, for example, toluene etc., and is added in an aqueous medium simultaneous or separately with a vinyl aromatic series monomer. the amount of the polymerization initiator used receives a vinyl aromatic series monomer 100 weight part — a 1.0 - 3.0 weight part — it is a 1.1 - 2.0 weight part preferably. Shock resistance with a foaming fabrication object peculiar to about [that rigidity is not improved] and polyethylene system resin with which the diameter of a distributed particle of the vinyl aromatic series polymer in the property modification polyethylene system resin particles obtained is large, carries out preliminary foaming of this particle, carries out hot forming further, and is obtained is spoiled under in 1.0 weight part. Even if it uses it exceeding 3.0 weight parts, since the molecular weight of a vinyl aromatic series polymer becomes small more than needed, it is not desirable.

By making the amount of polymerization initiators into a 1.0 - 3.0 weight part, it can be possible to make small the diameter of a distributed particle of the vinyl aromatic series polymer in generation polymerization particles, and to maintain at the molecular weight more than fixed, and the rigidity and shock resistance of a foaming fabrication object can be raised by leaps and bounds.

As soil suspension used in this invention, poorly soluble inorganic matters, such as water-soluble polymer substance; calcium phosphate, such as polyvinyl alcohol, a poly vinyl pylori boss, and methyl cellulose, pyrophoric acid magnesium, and magnesium oxide, and others are used.

Sinking in of a vinyl aromatic series monomer is performed under churning by heating under the conditions which the polymerization of this monomer does not start substantially. Although the higher one of sinking-in temperature is desirable from a point of sinking-in promotion, since the vinyl aromatic series monomer before sinking in polymerizes by **** decomposition of a polymerization initiator, proper temperature setting is required. the optimal sinking-in temperature which is alike and receives preparation vinyl aromatic series single **** can be set up by making a part for the increase in weight after polyethylene system resin of weight known is immersed in a lot of vinyl aromatic series monomers for 30 minutes into the amount of saturation sinking in in that temperature, and carrying out what point of this measurement under that temperature. About 3 hours is suitable for sinking-in time from 30 minutes. After sinking in of a vinyl aromatic series monomer, the temperature of water soil suspension is raised again and a vinyl aromatic series monomer is polymerized under churning. Generally under the temperature which decomposition of a polymerization initiator fully starts, polymerization time is 3 to 20 hours.

It is a thing with the character not to dissolve the generated property modification polyethylene system resin particles as a foaming agent used in this invention, or to make it swell slightly, and the thing of gas or a liquid is always used by normal pressure. For example, n-propane, n-butane, iso butane, n-pen tongue, an iso pen tongue, Resin fellows hydrocarbon, such as a neo pen tongue, n-hexane, and iso HEKISAN, Alicycle fellows hydrocarbon, such as cyclo butane and a cyclo pen tongue, and methyl chloride, these are independent at halogenated hydrocarbon, such as ethyl chloride, methylene chloride,

bird chloro fluoro methane, dichloro fluoro methane, dichloro difluoromethane, chloro difluoromethane, and dichloro tetrafluoro ethane, — or — two or more sorts are mixed It can use.

You may use like the above whichever of the method of depending the property modification polyethylene system resin particles which were obtained by carrying out as a method of carrying out preliminary foaming on steam which is well-known technology, and the method proposed in the West German publication of patent applications No. 2,107,683, a JP,56-1344,B number, etc. For example, the method of a JP,56-1344,B number distributes generation particles in an aqueous medium under existence of a volatile foaming agent and a suspension in a resisting pressure container. After heating in this state and infiltrating a volatile foaming agent into particles, while keeping constant this internal pressure inside a resisting pressure container in the state where it heated under the pressurization more than the steam pressure of a volatile foaming agent more than the apparent initial softening of these particles, it is water about this resisting pressure container to these particles. It emits to a low-pressure area.

It is filled up in the metallic mold which cannot be sealed although it can be closed down, heating weld is carried out, and the preliminary foaming particles which were obtained by carrying out like the above are used as a foaming fabrication object. The acquired foaming fabrication object has with a Charpy impact values of 1.0 or more high rigidity and the outstanding shock resistance the forming object density of 19g / above **.

[Function and Effect]

[this invention] by carrying out 1.0-3.0 weight part use of the polymerization initiator in which the straight chain-like low-density-polyethylene resin particles non-constructed a bridge are used, this monomer is polymerized to a vinyl aromatic series monomer 100 weight part, and it deals, as mentioned above The diameter of a distributed particle of the vinyl aromatic series polymer which exists in the resin particles generated after the polymerization is the method which about [of the diameter of a particle by 0.05-0.1 micrometer and the conventional method] 1/10 may be made to carry out micro distribution. It is the thing of the level which cannot be attained at all by simple blend with a natural thing.

The foaming fabrication object acquired by being filled up in the model which cannot be sealed although the property modification polyethylene system resin preliminary foaming particles manufactured by this invention can be closed, and carrying out hot forming, Compared with the polyethylene system resin foaming fabrication object in which property modification was carried out by the conventional vinyl aromatic series, it has higher rigidity and the outstanding shock resistance, and is used suitably for shock absorbing material, a packaging medium, a container, etc.

[Example]

Hereafter, although an example explains in more detail, this invention is not limited to these.

An example 1-5, comparative example 1-4 It is to the autoclave of content volume 3.5** as a pure water 400 weight part, the density of 0.93g/cm², the straight chain-like low-density-polyethylene resin particle (product made from Mitsui petrochemistry "ULTZEX 3021F") 100 weight part for MFR2.1g / 10 minutes, and soil suspension. An alpha olefin SURUFON acid soda 0.1 weight part, a tricalcium phosphate 3 weight part, Furthermore, what dissolved 1 of quantity shown in 1st table as polymerization initiator, 1-screw (tert-butyl peroxide) 3, 3, and 5-bird MECHIRUSHIKUROHEKISAN in the styrene monomer of the quantity shown in the 1st table was added and agitated, and it was considered as water soil suspension. Subsequently, this water soil suspension was held for 1 hour at the styrene monomer and the sinking-in temperature of a polymerization initiator which are shown in the 1st table, and the styrene monomer and the polymerization initiator were made to sink in into polyethylene resin particles.

Next, temperature of this water soil suspension was ****(ed) at 115 degrees C, it held at this temperature for 4 hours, and the polymerization was completed.

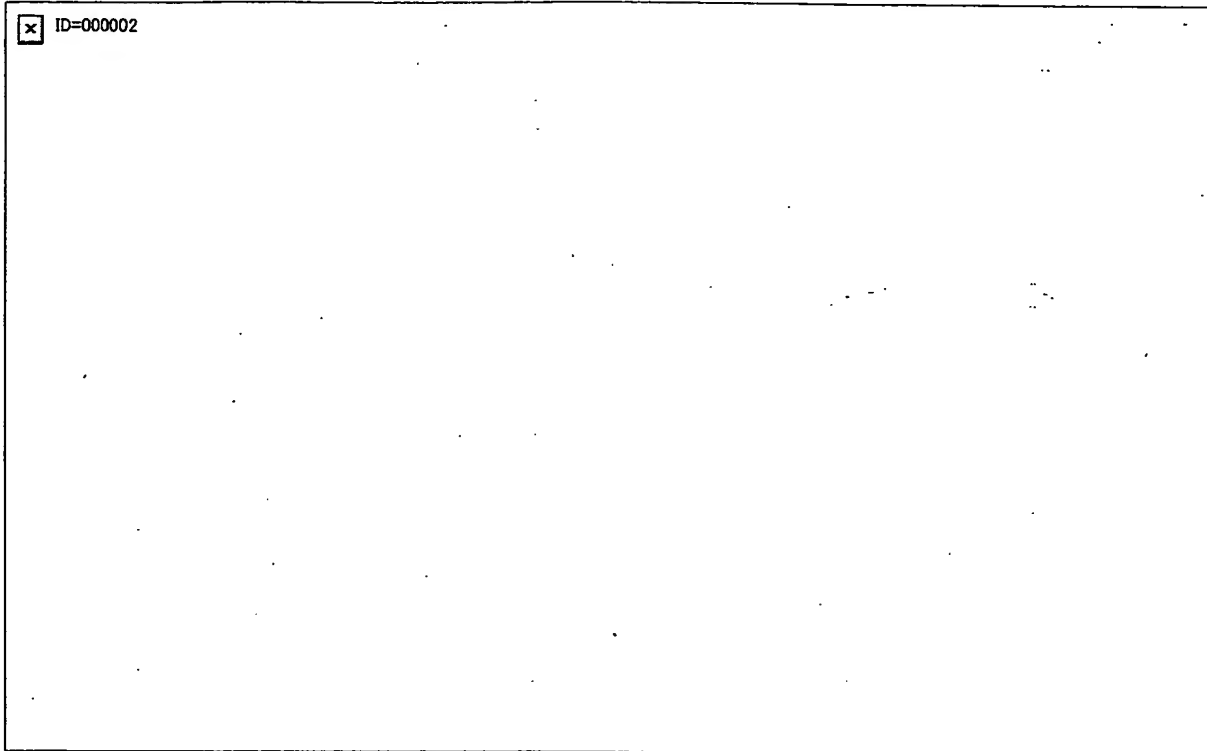
cooling and taking out resin particles, after pressing fit after cooling and a butane (n-butane 75% and iso butane 25%) 30 weight part to 70 degrees C and holding at this temperature for 1 hour — pickling — it washed and dried.

The obtained fizz particles were made to foam in steam, and the metallic mold which has many 300x170x40mm small holes which cannot be sealed although it can be closed down was filled up, and after pouring in steam of the pressure of 1.0 kgf/cm² from the small hole and heating it for 40 seconds, it cooled for 90 seconds and took out.

The density of the acquired foaming fabrication object, the degree of weld, compressive strength, and a Charpy impact value are shown in the 1st table.

An example 6-8, comparative example 5-7 Until it sets up as the quantity of the above-mentioned polymerization initiator and the quantity of a styrene monomer are shown in the 1st table, and it completes a polymerization It carried out like the ***** example and the comparative example, and

after that, it cooled to 60 degrees C, the dichloro difluoromethane 50 weight part was pressed fit, and it *** (ed) again, and held at 130 degrees C. Subsequently, it foamed by opening the end of a container wide, holding internal pressure to 30 kgf/cm² in N₂. The obtained preliminary foaming particles were fabricated like the example and the comparative example. The result of having evaluated the physical properties of the acquired foaming fabrication object is shown in the 1st table.



(**) (1) 50% compressive strength: It measured according to the JIS K 6767 method.

(2) Charpy impact value: By the 20x30x150mm specimen (with no notch), the Charpy examination machine was set as the hammer weight of 20kg, 124 hammer angles, and Sepang 90mm, and was measured.

(3) the degree of weld: a forming object — pulling — it judged in the state of destruction of the fracture surface when fracturing.

O : in less than 10 to 40%**particle surface exposure, less than 40 to 70%:particle surface exposure is [particle surface exposure / less than 10%O:particle surface exposure] 70% or more.

[Translation done.]

を第1表に示す。

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第 1 表

		ポリスチレン樹脂 粒子/スチレン 単 量 体 (重量比)	スチレン単量体 及び重合開始 剤の含浸 温度 (℃)	重合開始剤 部 数 (重量部)	予備発泡 粒子倍率	発泡成形 体 密 度 (g/cm ³)	発 泡 成 形 体 物 性		
							50%圧 縮強度	引張強 度	脆性度
実 施 例	1	100/10	40	1.1	4.0	2.3	1.9	2.8	○
	2	100/100	8.5	1.1	4.5	2.1	2.3	1.5	○
	3	100/100	8.5	2.5	4.0	2.3	2.2	1.4	○
	4	100/150	9.0	1.1	5.0	1.9	2.4	1.2	⊕
	5	100/300	9.5	1.1	5.0	2.0	2.5	1.0	⊕
	6	100/100	8.5	1.1	3.5	2.7	2.6	1.6	○
	7	100/150	9.0	1.1	4.5	2.1	2.3	1.2	○
	8	100/300	9.5	1.1	4.5	2.1	2.4	1.0	⊕
比 較 例	1	100/100	8.5	0.4	4.8	2.0	1.7	0.8	△
	2	100/100	8.5	0.8	4.2	2.3	1.8	0.9	○
	3	100/100	8.5	3.2	3.8	2.5	1.8	0.8	×
	4	100/350	9.8	1.1	5.0	2.0	2.0	0.4	○
	5	100/100	8.5	0.4	4.0	2.4	1.9	0.7	△
	6	100/100	8.5	0.8	3.8	2.5	2.0	0.8	○
	7	100/100	8.5	3.2	3.5	2.8	2.0	0.9	×

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⑮ 発明の名称 改質ポリエチレン系樹脂予備発泡粒子の製造方法

⑯ 特 願 昭63-115397

⑰ 出 願 昭63(1988)5月12日

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明 細 書

1. 発明の名称

改質ポリエチレン系樹脂予備発泡粒子の製造方法

2. 特許請求の範囲

1. ポリエチレン系樹脂粒子100重量部、ビニル芳香族単量体5～300重量部及び該単量体100重量部に対し1.0～3.0重量部の重合開始剤を水性媒体中に分散させ、該単量体の重合が實質的におこなない温度に加熱して該単量体を前記ポリエチレン系樹脂粒子の内部及び表面に含浸せしめた後、上記水性懸濁液の温度を上昇させて該単量体の重合を行い、重合中もしくは重合終了後に揮発性発泡剤を含浸せしめ発泡させることを特徴とする改質ポリエチレン系樹脂予備発泡粒子の製造方法。

2. ビニル芳香族単量体がポリエチレン系樹脂粒子100重量部に対して30～200重量部である請求項1記載の製造方法。

3. 重合開始剤がビニル芳香族単量体100重

量部に対して1.1～2.0重量部である請求項1又は2記載の製造方法。

3. 発明の詳細な説明

(産業上の利用分野)

本発明は改質されたポリエチレン系樹脂予備発泡粒子の製造方法に関し、更に詳しくは、剛性及び耐衝撃性の極めて優れた発泡成形体を与える改質ポリエチレン系樹脂予備発泡粒子の製造方法に関する。

(従来技術)

一般に、ポリエチレン系樹脂の発泡体は弾性が高く、繰り返し応力に対しても逆の回復力が大きいという特徴の他に、耐油性、耐衝撃性に優れるという長所を有しており、重要な包装資材として広く利用されている。しかし、ポリエチレン系樹脂粒子を予備発泡粒子となし、これを型内成形して発泡成形体を得る場合、ポリエチレンの剛性の低さからその予備発泡粒子や型内成形後の発泡成形体の収縮が occur やすく、また得られた発泡成形体は柔らかく、圧縮強度が低いという短所を

有している。

このような欠点を改良する方法として、ポリエチレン系樹脂にビニル芳香族モノマーを含浸させて重合を行い、改質ポリエチレン系樹脂予備発泡粒子を得るという方法が特公開45-32623号、同51-46138号、同52-10150号、同59-3487号等により提案されている。しかし、これらの方法ではビニル芳香族単量体のポリエチレン系樹脂への含浸と重合が同時平行的に行われるため、粒子表面と内部とで重合反応において不均一性が生じ、その結果生成粒子の均質性が劣り、またポリエチレン系樹脂に含浸される前に無視しえない量の該単量体が単独粒子として重合してしまうという問題がある。

これらの問題を解決するために特公開58-53003号、同58-51009号、同58-51010号では、ビニル系単量体及び該単量体100重量部に対し0.01~0.8重量部の重合開始剤をポリエチレン系樹脂粒子に含浸重合する際、重合開始剤の分解が実質的におこらない温度で該

単量体の80%以上を含浸させた後、温度を上昇させて重合を行うという方法が開示されている。

この方法によれば、含浸工程と重合工程を分離することにより生成粒子の均質性が向上し、ビニル系単量体の単独重合物が事実上生成しないことが記載されている。

(発明が解決しようとする問題点)

上記の如くビニル系単量体をポリエチレン系樹脂粒子に含浸重合して得られる生成粒子は、ポリエチレン系樹脂のマトリックス中にビニル系重合体粒子が分散している得意構造を有しているが、従来技術による場合は、ビニル系重合体の分散粒子径が大きく、該生成粒子を予備発泡し、更に加熱成形して得られる発泡成形体は剛性、耐衝撃性ともに満足し得るものではない。

(問題点を解決するための手段)

本発明は、ポリエチレン系樹脂本来の性質である耐衝撃性に優れ、且つ剛性を改良した発泡成形体を与える改質ポリエチレン系樹脂予備発泡粒子を製造することを目的とし、ビニル芳香族単量体

を重合させる重合開始剤の量を該単量体100重量部に対し、1.0~3.0重量部使用して生成粒子中のビニル芳香族重合体の分散粒子径を小さくすることにより、優れた耐衝撃性及び剛性を備えた成形体を与える改質ポリエチレン系樹脂予備発泡粒子を製造する方法を提供するものである。

即ち、本発明はポリエチレン系樹脂粒子100重量部、ビニル芳香族単量体5~300重量部及び該単量体100重量部に対し1.0~3.0重量部の重合開始剤を水性媒体中に分散させ、該単量体の重合が実質的におこらない温度に加熱して該単量体を前記ポリエチレン系樹脂粒子の内部及び表面に含浸せしめた後、上記水性懸濁液の温度を上昇させて該単量体の重合を行い、重合中もしくは重合終了後に厚発性発泡剤を含浸せしめ発泡させることを特徴とする改質ポリエチレン系樹脂予備発泡粒子の製造方法を内容とするものである。

本発明において使用されるポリエチレン系樹脂としては、低密度ポリエチレン、直鎖状低密度ポリエチレン、高密度ポリエチレン、エチレン・ブ

ロピレン共重合体、エチレン・プロピレン・ブテン-1共重合体、エチレン・酢酸ビニル共重合体、エチレン・アクリル酸共重合体、エチレン・塩化ビニル共重合体、これらの2種以上の混合物等が挙げられる。上記直鎖状低密度ポリエチレンとしてはエチレンと α -オレフィンとの共重合体が好きましい。 α -オレフィンとしては例えば1-ブテン、1-ペンテン、1-ヘキセン、3-ジメチル-1-ブテン、4-メチル-1-ペンテン、4-ジメチル-1-ペンテン、1-オクテン等が挙げられる。これらのポリエチレン系樹脂は架橋されていてもよい。形状はパウダー、ペレット状等の粒子状態であることが好ましい。その平均粒径は0.05~5 μ m程度が好適な範囲である。0.05 μ mより小さい場合は発泡剤の逸散が激しく、5 μ mを超える大きな粒子を用いた場合は重合時の分散が困難であり、また成形時の充填性が悪くなるため好ましくない。

本発明において使用されるビニル芳香族単量体としては、スチレンの他にメチルスチレン、ジメ

チルスチレン、エチルスチレン、イソプロピルスチレン、クロルスチレン等の塩置換スチレン、 α -メチルスチレン等の α -置換スチレン等を単独又は2種以上の混合物、あるいは上記単量体と共重合可能な少量の他の単量体、例えばアクリロニトリル、アクリル酸エステル、メタクリル酸エステル、ジビニルベンゼン、マレイン酸モノまたはジアルキル、その他との混合物が使用される。

ビニル芳香族単量体の量は、ポリエチレン系樹脂100重量部に対して5~300重量部、好ましくは30~200重量部である。300重量部を超えると、ビニル芳香族単量体がポリエチレン系樹脂に均一に全部吸収されず、吸収されない単量体が単独で重合してしまうため好ましくない。また多量にビニル芳香族単量体を吸収したポリエチレン系樹脂は、ポリエチレン特有の性質を失う結果となる。一方、ビニル芳香族単量体が5重量部未満では、ポリエチレン系樹脂の剛性の改良が十分なされないため好ましくない。

本発明において用いられる重合開始剤としては、

一般にビニル芳香族単量体の懸濁重合開始剤として用いられているものをそのまま使用できる。例えば、ベンゾイルパーオキサイド、ラウロイルパーオキサイド、1-ブチルパーオキサイド、1-ブチルパーオキシベンゾエート、1,1-ビス(1-ブチルパーオキシ)3,3,5-トリメチルシクロヘキサノール、1-ブチルパーオキシイソプロピルカーボネート、2,2-ビス(1-ブチルパーオキシ)ブタン、ジタミルパーオキサイド等の有機過酸化物；アゾイソプロピロニトリル、アジビスジメチルパレロニトリル等のアゾ化合物等である。これらの重合開始剤は単独または2種以上併用して用いてもよい。重合開始剤は油性であるべきであり、ビニル芳香族単量体に溶解させるか、又は重合反応に支障をきたさない少量の溶剤、例えばトルエン等に溶解させてビニル芳香族単量体と同時に又は別々に水性媒体中に添加される。重合開始剤の使用量は、ビニル芳香族単量体100重量部に対し1.0~3.0重量部、好ましくは1.1~2.0重量部である。1.0重量部未満では、得られ

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る改質ポリエチレン系樹脂粒子中のビニル芳香族重合体の分散粒子径が大きく、該粒子を予備発泡し、更に加熱成形して得られる発泡成形体は剛性が改良されないばかりか、ポリエチレン系樹脂特有の耐衝撃性が損なわれる。3.0重量部を超えて使用しても、必要以上にビニル芳香族重合体の分子量が小さくなるため好ましくない。

重合開始剤量を1.0~3.0重量部にすることによって、生成重合粒子中のビニル芳香族重合体の分散粒子径を小さくし、また一定以上の分子量に保つことが可能で、発泡成形体の剛性及び耐衝撃性を飛躍的に向上させることができる。

本発明において用いられる懸濁剤としては、ポリビニルアルコール、ポリビニルピロリドン、メチルセルロース等の水溶性高分子物質；リン酸カルシウム、ピロリン酸マグネシウム、酸化マグネシウム等の難溶性無機物質、その他が使用される。

ビニル芳香族単量体の含浸は、攪拌下に該単量体の重合が實質的におこらない条件下で加熱して行われる。含浸温度は高いほうが含浸促進の点か

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らは好ましいが、重合開始剤の過早分解によって含浸前のビニル芳香族単量体が重合してしまうので、適正な温度設定が必要である。重量増分のポリエチレン系樹脂を大量のビニル芳香族単量体に30分間浸漬した後の重量増加分をその温度での飽和含浸量とし、何点かの温度下でこの測定をすることにより、仕込みビニル芳香族単量体に対する最適含浸温度を設定することができる。含浸時間は30分から3時間程度が好適である。

ビニル芳香族単量体の含浸後、水性懸濁液の温度を再び上昇させて攪拌下にビニル芳香族単量体の重合を行う。重合開始剤の分解が十分におこる温度下で、重合時間は一般に3~20時間である。

本発明において用いられる発泡剤としては、生成した改質ポリエチレン系樹脂粒子を溶解しないか、又は僅かに膨潤させるにすぎない性質を持ったもので、常温常圧で気体もしくは液体のものが用いられる。例えばn-プロパン、n-ブタン、イソブタン、n-ペンタン、イソペンタン、ネオペンタン、n-ヘキサン、イソヘキサン等の脂肪

族炭化水素類、シクロブタン、シクロペンタン等の脂環族炭化水素類、及びメチルクロライド、エチルクロライド、メチレンクロライド、トリクロフルオロメタン、ジクロロフルオロメタン、ジクロロジフルオロメタン、クロロジフルオロメタン、ジクロロテトラフルオロエタン等のハロゲン炭化水素類で、これらは単独又は2種以上混合して用いることができる。

上記の如くして得られた改質ポリエチレン系樹脂粒子を予備発泡させる方法としては、公知技術である水蒸気による方法と西独公開特許公報第2,107,683号、特公昭56-1344号等で提案されている方法のどちらを用いてもよい。例えば特公昭56-1344号の方法は、生成粒子を耐圧容器中で揮発性発泡剤と懸濁剤の存在下で水性媒体中に分散させ、この状態で加熱し揮発性発泡剤を粒子中に含浸させた後、揮発性発泡剤の蒸気圧以上の加圧下で該粒子の軟化温度以上に加熱した状態で該耐圧容器内圧を一定に保ちながら、該耐圧容器から該粒子を水と共に低圧域に放出す

るというものである。

(作用・効果)

本発明は、上述したように、ビニル芳香族単量体100重量部に対し該単量体を重合させる重合開始剤を1.0~3.0重量部使用することによって、重合後生成した樹脂粒子中に存在するビニル芳香族重合体の分散粒子径が0.05~0.1 μ mと従来法による粒子径の10分の1程度にまでマイクロ分散せうする方法であり、当然のことながら単独ブレンドでは到底達成しえないレベルのものである。

本発明により製造される改質ポリエチレン系樹脂予備発泡粒子を閉鎖しうるが密閉しえない型内に充填し、加熱成形して得られる発泡成形体は、従来のビニル芳香族により改質されたポリエチレン系樹脂発泡成形体に比べ、より高い剛性と優れた耐衝撃性を有し、緩衝材、包装材、容器等に好適に用いられる。

(実施例)

以下、実施例により更に詳しく説明するが、本

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発明はこれらに限定されるものではない。

実施例1~5、比較例1~4

内容積3.5ℓのオートクレーブに純水400重量部、密度0.93g/cm³、MFR2.1g/10分の直鎖状低密度ポリエチレン樹脂粒子(三井石油化学製「ウルトゼックス3021P」)100重量部、懸濁剤として α -オレフィンスルホン酸ソーダ0.1重量部、リン酸三カルシウム3重量部、更に重合開始剤として第1表に示す量の1、1-ビス(1-ブチルパーオキシ)3,3,5-トリメチルシクロヘキサンを、第1表に示す量のステレン単量体に溶解したものを加えて攪拌し、水性懸濁液とした。

次いで、この水性懸濁液を第1表に示すステレン単量体及び重合開始剤の含浸温度で1時間保持し、ステレン単量体及び重合開始剤をポリエチレン樹脂粒子中に含浸せしめた。

次に、この水性懸濁液の温度を115℃に昇温し、該温度で4時間保持して重合を完結させた。

70℃まで冷却後、ブタン(n-ブタン75%

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イソブタン25%)3.0重量部を圧入し該温度で1時間保持した後、冷却して樹脂粒子を取り出し、酸洗、水洗、及び乾燥した。

得られた発泡性粒子を水蒸気中で発泡させ、300×170×40mmの閉鎖しうるが密閉しえない、多数の小孔を有する金型に充填し、1.0kg/cm²の圧力の水蒸気を小孔から注入し40秒加熱した後、90秒冷却して取り出した。

得られた発泡成形体の密度、融着度、圧縮強度、シャルピー衝撃値を第1表に示す。

実施例6~8、比較例5~7

上記重合開始剤の量及びステレン単量体の量を第1表に示す如く設定し、重合を完結させるまでは上記実施例及び比較例と同様に行い、その後、60℃まで冷却してジクロロフルオロメタン50重量部を圧入し再び昇温して130℃に保持した。次いで、N₂にて内圧を3.0kg/cm²に保持しながら容器の一端を開放して発泡を行った。得られた予備発泡粒子を実施例、比較例と同様に成形した。得られた発泡成形体の物性を評価した結果

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を第 1 表に示す。

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第 1 表

		ポリブチレン樹脂 粒子/ポリブチレン 単 量 体 (重量比)	ポリブチレン単量体 及び重合開始 剤の含浸 温度 (℃)	重合開始剤 部 数 (重量部)	予備発泡 粒子倍率	発泡成形 体 密 度 (g/cm ³)	発 泡 成 形 体 物 性		
							50%圧 縮強度	シャルピー 衝撃値	融着度
実 施 例	1	100/10	40	1.1	4.0	2.3	1.9	2.8	○
	2	100/100	8.5	1.1	4.5	2.1	2.3	1.5	○
	3	100/100	8.5	2.5	4.0	2.3	2.2	1.4	○
	4	100/150	9.0	1.1	5.0	1.9	2.4	1.2	◎
	5	100/300	9.5	1.1	5.0	2.0	2.5	1.0	◎
	6	100/100	8.5	1.1	3.5	2.7	2.6	1.6	○
	7	100/150	9.0	1.1	4.5	2.1	2.3	1.2	○
	8	100/300	9.5	1.1	4.5	2.1	2.4	1.0	◎
比 較 例	1	100/100	8.5	0.4	4.8	2.0	1.7	0.8	△
	2	100/100	8.5	0.8	4.2	2.3	1.8	0.9	○
	3	100/100	8.5	3.2	3.8	2.5	1.8	0.8	×
	4	100/350	9.8	1.1	5.0	2.0	2.0	0.4	○
	5	100/100	8.5	0.4	4.0	2.4	1.9	0.7	△
	6	100/100	8.5	0.8	3.8	2.5	2.0	0.8	○
	7	100/100	8.5	3.2	3.5	2.8	2.0	0.9	×

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(注) (i) 50%圧縮強度:

JIS K 6767法に従って測定した。

(ii) シャルビー衝撃値:

20×30×150 mmの試験片(ノッチなし)

でシャルビー試験器をハンマー重量20kg、

ハンマー角度124度、スパン90mmに設定

して測定した。

(iii) 脆着度:

成形体を引張りにより破断した時の破断面の破壊状態で判断した。

◎: 粒子表面露出が10%未満

○: " 10~40%未満

△: " 40~70%未満

×: " 70%以上

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